



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : C08F 4/28, 4/34, 26/10 C08F 220/08	A1	(11) International Publication Number: WO 91/03496 (43) International Publication Date: 21 March 1991 (21.03.91)
(21) International Application Number: PCT/US90/04321 (22) International Filing Date: 3 August 1990 (03.08.90) (30) Priority data: 401,682 1 September 1989 (01.09.89) US (71) Applicant: GAF CHEMICALS CORPORATION [US/ US]; 1361 Alps Road, Wayne, NJ 07470 (US). (72) Inventor: TAZI, Mohammed ; 33 Claremont Terrace, Wayne, NJ 07470 (US). (74) Agents: MAUE, Marilyn, J. et al.; GAF Corporation, 1361 Alps Road, Building No. 10, Wayne, NJ 07470 (US).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent)*, DK (European patent), ES (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERIZATION PROCESS USING TERTIARY-AMYLPEROXY PIVALATE AS THE FREE RADICAL INITIATOR (57) Abstract Free radical polymerization of monomers in the presence of t-amylperoxy pivalate as the free radical initiator is described. Copolymers of maleic anhydride and a vinyl monomer, e.g. a C ₁ -C ₅ alkyl vinyl ether, and water soluble polyvinylpyrrolidone, are representative polymers prepared in accordance with the process of the invention.		

DESIGNATIONS OF "DE"

Until further notice, any designation of "DE" in any international application whose international filing date is prior to October 3, 1990, shall have effect in the territory of the Federal Republic of Germany with the exception of the territory of the former German Democratic Republic.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MC	Monaco
AU	Australia	FI	Finland	MG	Madagascar
BB	Barbados	FR	France	ML	Mali
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GR	Greece	NL	Netherlands
BJ	Benin	HU	Hungary	NO	Norway
BR	Brazil	IT	Italy	PL	Poland
CA	Canada	JP	Japan	RO	Romania
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	LI	Liechtenstein	SN	Senegal
CM	Cameroon	LK	Sri Lanka	SU	Soviet Union
DE	Germany	LU	Luxembourg	TD	Chad
DK	Denmark			TG	Togo
				US	United States of America

POLYMERIZATION PROCESS USING TERTIARY-AMYLPEROXY
PIVALATE AS THE FREE RADICAL INITIATOR

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to a process for making polymers, and, more particularly, to a polymerization process using t-amylperoxy pivalate as the free radical initiator.

2. Description of the Prior Art

Free radical initiators used in polymerization processes at elevated temperatures have included alkyl peresters, dialkyl peroxides, perketals, peroxydicarbonates, hydroperoxides, azo compounds and carbon-carbon labile compounds. Copolymerization also has been carried out at relatively low temperatures, e.g. room temperature, using a redox catalyst, such as, a combination of a redox catalyst and ascorbic acid, or, of a peroxydicarbonate and benzoin. It has been possible also to employ the polymerization initiator conjointly with a suitable accelerator, for example, an amine derived from a cyclic or phenyl structure, the amine being used by itself or together with an organic compound of a transition metal. Copolymerization also has been carried out with a mixture of different polymerization initiators having different decomposition temperatures.

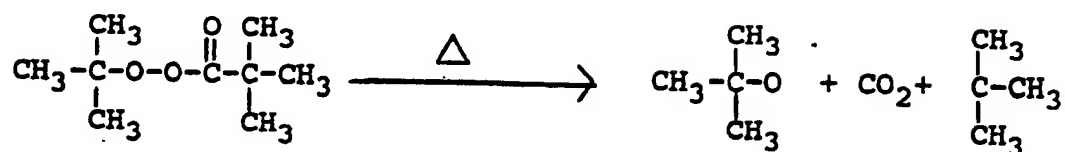
- 2 -

The following compounds have been employed in free radical initiated polymerizations: acetyl cyclohexane-sulfonyl peroxide, diacetyl peroxydicarbonate, dicyclohexyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate, tert-butyl per[oxy]-neodecanoate, 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile); tert-butylperoxy pivalate, dioctanoyl peroxide, dilauroyl peroxide, 2,2'-azobis-(2,4-dimethylvaleronitrile), tert-butylazo-2-cyanobutane; dibenzoyl peroxide, tert-butyl per[oxy]-2-ethylhexanoate, tert-butyl per[oxy]maleate, 2,2-azobis(isobutyronitrile); bis(tert-butylperoxy)cyclohexane, tert-butylperoxyisopropyl carbonate, tert-butyl per[oxy]acetate; 2,2-bis(tert-butylperoxy)butane, dicumyl peroxide, di-tert-amyl peroxide, di-tert-butyl peroxide, pinane hydroperoxide, cumene hydroperoxide, and tert-butyl hydroperoxide.

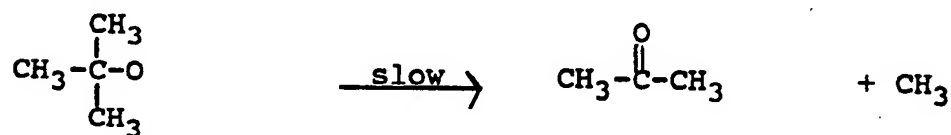
These polymerization initiators are used in amounts of about 0.05 to 10% by weight of the monomers, and, preferably about 0.1 to 5% by weight of an initiator is required.

t-Butylperoxy pivalate (TBPP) is a widely used free radical polymerization initiator: see U.S. patents 3,624,123; 3,887,528 and 4,237,257. TBPP undergoes thermal homolysis to produce t-butoxy and t-butyl free radicals.

Thermal Homolysis of TBPP



whereupon β -scission of the t-butoxy radical produces the methyl free radical:



Thus, the active free radical species for initiation of free radical polymerization are:

Active Free Radical Species of TBPP

$\text{CH}_3\cdot$ methyl radical

$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3-\text{C}-\text{O}\cdot \\ | \\ \text{CH}_3 \end{array}$ t-butoxy radical

$\begin{array}{c} \text{CH}_3\cdot \\ | \\ \text{CH}_3-\text{C} \\ | \\ \text{CH}_3 \end{array}$ t-butyl radical

- 4 -

The methyl and t-butoxy free radicals, respectively, have high bond dissociation energies (BDE) of 104 and 105 kcal/mole. This means that these radicals can readily abstract a labile hydrogen atom from the polymer to convert an otherwise linear polymer into branched polymers which have lower water solubility and lower molecular weights than the linear polymers. In addition, the half-life of TBPP initiator, i.e. the time at a given temperature to effect a loss of one-half of the perester's active oxygen content, is a lengthy 24.6 hours at 50°C. Accordingly, TBPP requires a high reaction temperature, e.g. 60°-80°C., to carry out the polymerization within a reasonable period of time.

Accordingly, it is an object of this invention to provide polymerization processes using a free radical initiator whose thermal homolysis reaction provides free radicals which undergo rapid β -scission to produce active free radical species which are weak hydrogen abstractors, and, thus enable the formation of linear polymers having high degree of water solubility and high molecular weights.

SUMMARY OF THE INVENTION

A free radical initiated polymerization process is described herein in which at least one monomer is polymerized in the presence of t-amylperoxy pivalate as the free radical initiator. Representative polymerizations using the t-amylperoxy pivalate initiator of the invention include the copolymerization of maleic anhydride and a C₁-C₅ alkyl vinyl ether to produce 1:1 alternating copolymers, and the homopolymerization of vinyl pyrrolidone to form high molecular weight polyvinyl pyrrolidone.

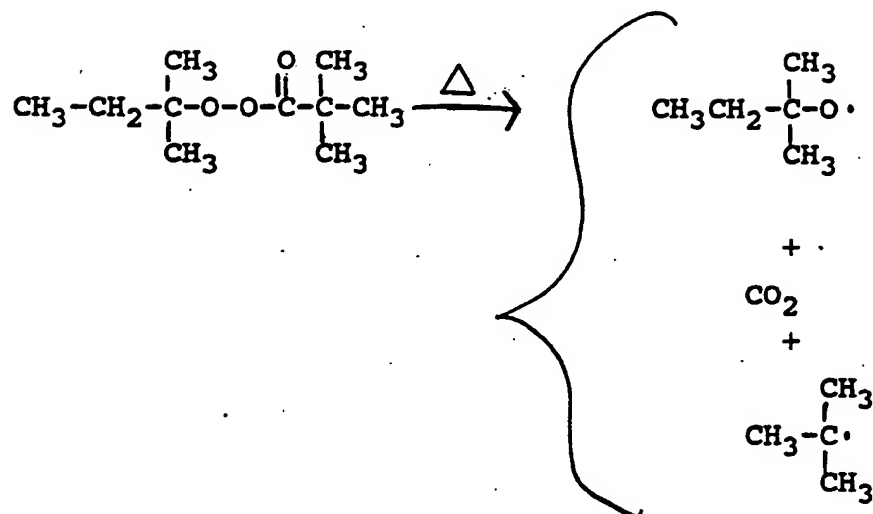
- 5 -

The polymerization processes of the invention are carried out at a faster reactivity rate, and at a lower temperature, than the same polymerizations using related free radical initiators. The process herein may provide linear polymers of high molecular weight, as contrasted to branched polymers of low molecular weight, formed with other initiators.

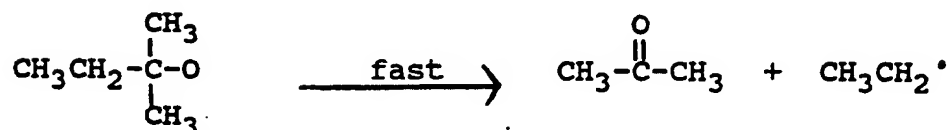
DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, a free radical polymerization process is provided herein in which t-amylperoxy pivalate (TAPP) is used as the free radical polymerization initiator. TAPP undergoes thermal homolysis as follows:

- 6 -

Thermal Homolysis of TAPP

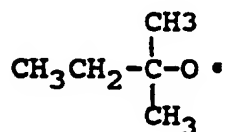
followed by β -scission of the t-amyloxy radical:



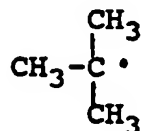
Accordingly the active free radical species of TAPP are:



ethyl radical



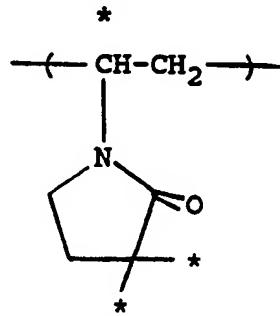
t-amyloxy radical



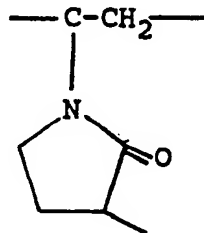
t-butyl radical

The ethyl and t-amyloxy free radical has a BDE of only 98 kcal/mole, and is therefore a relatively weak hydrogen abstractor. Thus, linear polymers can be provided using the TAPP initiator of the invention.

For example, polyvinylpyrrolidone (PVP) formed by free radical polymerization of vinyl pyrrolidone has several active hydrogen sites indicated by the asterisks for hydrogen abstraction, by active free radical species of TBPP



which would product branched PVP polymers:



whereas TAPP, having weak hydrogen abstractors can produce more nearly linear PVP polymers having increased water dissolution.

The invention will now be described by reference to the following examples.

- 8 -

Furthermore, it is known that lower molecular weight polymers are produced when high polymerization temperatures or long reaction periods are required. TAPP, as compared to TBPP, can effect completed polymerizations at lower temperatures, and/or with shorter reaction periods, it is possible also to produce higher molecular weight polymers than hitherto achieved.

Suitably, the t-amylperoxy pivalate initiator of the invention may be used in free radical initiated polymerizations where at least one monomer is polymerized in the presence of a free radical initiator. Representative free radical polymerizations include the preparation of maleic anhydride-based polymers, e.g. copolymerization of maleic anhydride with C₁-C₅ alkyl vinyl ethers, with styrene, and/or with acrylic acid; the preparation of polyvinylpyrrolidone by the homopolymerization of vinyl pyrrolidone, and for other free radical polymerizations well known in the art.

The t-amylperoxy pivalate initiator is employed in these polymerizations in an amount of about 0.01 to 10% by wt. of the monomers, preferably about 0.1 to 5%.

The polymers produced using the TAPP initiator are characterized by being more water soluble (more linear, less branched), of controlled (lower) viscosity (higher molecular weight) and with less residual monomer (< 1000 ppm, higher purity, less toxic) than the same polymers made with other, even closely related free radical initiators.

The t-amylperoxy pivalate may be obtained from the Pennwalt Corp. under their commercial name of Lupersol 554M75, which is a 75% by wt. active solution in odorless mineral spirits.

- 9 -

EXAMPLE 1Preparation of Polyvinylpyrrolidone

A 2-liter reactor was provided with agitation, gas inlet, condenser, and thermocouple and was charged with 270 g. (2.3 moles) of non-stabilized vinyl pyrrolidone monomer, buffered with 0.27 g. of tetrasodium pyrophosphate and 1,080 g. of deionized water. The reactor was swept clean of oxygen by admitting nitrogen gas through the inlet tube. Then the reactor was heated to 55°C. and 0.25 g. of t-amylperoxy pivalate was added (< 0.1% by wt. of vinyl pyrrolidone). The reaction was carried out at 56°-59°C. for 5 hours. Then an additional 0.25 g. of TAPP was added and the reaction continued for 2 hours. At the end of the reaction period, the reaction product included 21% solids with a residual monomer content of only 0.04%. The PVP polymer product in water was characterized by a K-value of 121; a Brookfield viscosity of 120,000 cps at 26°C. and excellent water dissolution.

EXAMPLE 2Preparation of Copolymers of
Maleic Acid and Methyl Vinyl Ether

A 1-liter pressure reactor was charged with 63.8 g. of methyl vinyl ether and 143 g. of acetone. A solution of 98 g. of maleic anhydride in 147 g. of acetone was prepared and charged into a syringe pump. The reactor was heated until the temperature of the charge reached 55°C. Then 0.94 g. of t-amylperoxy pivalate (1% by wt. of maleic anhydride) was introduced in 20 ml. of the maleic anhydride solution in one shot. Thereafter, the rest of

- 10 -

the solution was fed into the reactor continuously over a 4-hour period. Afterwards, the reaction mixture was held at 55°C. for an hour and the reactor was cooled to 25°-30°C. Excess methyl vinyl ether was removed and collected. The reaction product was discharged as a solution of maleic anhydride - methyl vinyl ether copolymer in acetone. The specific viscosity of the product at 25°C. was 0.38 as measured in 2-butanone (1% solution).

EXAMPLE 3

The procedure of Example 1 was followed to make PVP, using t-butylperoxy pivalate in place of t-amylperoxy pivalate. The product had a K-value of only 112; a residual monomer content of 0.14%, and relatively poor water dissolution.

EXAMPLE 4

The procedure of Example 2 was followed using t-butylperoxy pivalate. The specific viscosity of the copolymer was only 0.25.

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made which are within the skill of the art. Accordingly, it is intended to be limited by the appended claims only, in which:

WHAT IS CLAIMED IS:

1. A free radical initiated polymerization process which comprises effecting polymerization of at least one monomer in the presence of t-amylperoxy pivalate as the free radical initiator.
2. A polymerization process which comprises copolymerizing maleic anhydride and a C₁-C₅ alkyl vinyl ether in the presence of t-amylperoxy pivalate as a free radical initiator.
3. A polymerization process for making polyvinylpyrrolidone which comprises polymerizing vinyl pyrrolidone in the presence of t-amylperoxy pivalate as a free radical initiator.
4. A polymerization process according to claim 2 wherein the reaction temperature is about 55°-85°C.
5. A polymerization process according to claim 2 wherein the polymerization is carried out in a solvent.
6. A polymerization process according to claim 5 wherein said solvent is a ketone, ester, ether, aliphatic hydrocarbon, aromatic hydrocarbon, or aliphatic chlorinated hydrocarbon.

- 12 -

7. A polymerization process according to claim 6 wherein said solvent is acetone.

8. A polymerization process according to claim 6 wherein said initiator comprises about 1-10% by weight of maleic anhydride present.

9. A polymerization process according to claim 3 in which the reaction temperature is about 56°-59°C.

10. A polymerization process according to claim 9 wherein polymerization is carried out in water.

11. A polymerization process according to claim 10 wherein the PVP polymer product in water has a 21% solids content, a K-value of 121, a Brookfield viscosity of 120,000 cps at 26°C., and a residual monomer content of about 0.04% or less.

12. A polymerization process according to claim 3 wherein said initiator is present in an amount of about 0.1 to 10% by wt. of vinyl pyrrolidone monomer present.

- 13 -

13. A polymerization process according to claim 12 wherein the initiator level is about 0.5 to 2%.

14. A polyvinyl pyrrolidone composition in water at about 21% solids having a PVP K value of about 12, a Brookfield viscosity of 120,000 cps at 26°C., and a residual monomer content of about 0.04% or less.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US90/04321

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 IPC (5): C08F 4/28, 4/34, 26/10, 220/08
 U.S. CL. 526/227, 264, 317.1

II. FIELDS SEARCHED

Minimum Documentation Searched ⁷

Classification System

Classification Symbols

U.S.

526/227, 264, 317.1

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched ⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹

Category ^a	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
<u>X</u> Y	US, A, 4,818,794 (DENZINGER ET AL) 04 APRIL 1989: See column 3, lines 38-39.	<u>1</u> 2, 4-8
Y	US, A, 4,613,483 (COHEN) 23 SEPTEMBER 1986 See the entire document.	2, 4-8
Y	US, A, 4,816,534 (NUBER ET AL) 28 MARCH 1989 See the entire document.	3, 9-12

^a Special categories of cited documents: ¹⁰

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search

22 OCTOBER 1990

Date of Mailing of this International Search Report

24 JAN 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

Thomas McDonald, Jr.

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

V. ☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE¹

This International search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1. ☐ Claim numbers _____, because they relate to subject matter ¹²not required to be searched by this Authority, namely:

2. ☐ Claim numbers _____, because they relate to parts of the International application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out ¹³, specifically:

3. ☐ Claim numbers _____, because they are dependent claims not drafted in accordance with the second and third sentences of PCT Rule 6.4(a).

VI. ☒ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING²

This International Searching Authority found multiple inventions in this International application as follows:

- I. Claims 1, 2, 4-8, drawn to a polymerization process comprising copolymerizing maleic anhydride and a C₁-C₅ alkyl vinyl ether; classified in Class 526 Subclass 317.1.
 - II. Claims 1, 3, 9-12, drawn to a polymerization process for making polyvinylpyrrolidone; classified in Class 526****
1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application. Telephone practice (see attachment).
 2. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

 3. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

 4. ☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

- ☐ The additional search fees were accompanied by applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

Con't. from PCT/ISA/210 supplemental sheet (2).

**** Subclass 264.

The international application lacks unity of invention under PCT Rule 13 because of the following reason:

Inventions I and II do not form a single inventive concept because they are drawn to two mutually exclusive species of polymerization process and are thus different inventions (claim 1 is generic to both processes).